(12) UK Patent Application (19) GB (11) 2 253 848 (13) A

(43) Date of A publication 23.09.1992

(21) Application No 9204887.5

(22) Date of filing 05.03.1992

(30) Priority data
(31) 9105677 (32) 19.03.1991 (33) GB

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(51) INT CL[5]
C07D 209/18, A01N 43/38, C07D 209/30

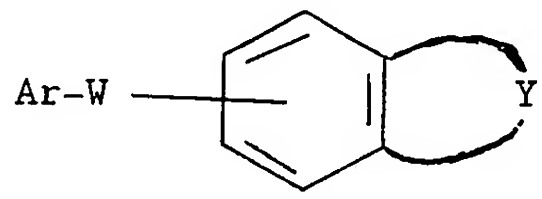
(52) UK CL (Edition K)
C2C CAA CBD CMB C1343 C200 C213 C22Y C220 C25Y C250 C251 C31Y C311 C313 C326 C337 C338 C36Y C364 C366 C367 C368 C376 C38Y C43X C440 C490 C491 C62Y C624 C628 C65X C656 C658 C662 C672 C676 C694 C697 C80Y C805
U1S S1306

(56) Documents cited
GB 1403559 A
CA 113 (3): 23510 g

(58) Field of search
UK CL (Edition K) **C2C CBD CMB**
INT CL[5] **C07D 209/18 209/30**
Online databases: CAS ONLINE

(54) Heterocyclic compounds

(57) A compound of formula (I):



(I)

in which Ar is an optionally substituted aryl or heterocyclic ring system;
W is O or NR^1 where R^1 is hydrogen or lower alkyl or alkenyl;
Y is a 5 membered ring containing one nitrogen atom, the ring being substituted by a group $CR^2R^3XR^4$ and optionally by one or more additional groups; X is $(CH_2)_n$, CH=CH, $CH(OR^6)CH_2$, $COCH_2$; where n is 0, 1 or 2; R^2 and R^3 are H, optionally substituted alkyl, alkenyl or alkynyl, halogen, NR^7R^8 or R^2 and R^3 together with the carbon to which they are attached form an optionally substituted alkenyl or cycloalkyl group;
R^4 is CO_2R^9, CN, COR^9, CH_2OR^9, $CH(OH)R^9$, $CH(OR^9)R^{10}$, $CSNH_2$, $COSR^9$, $CSOR^9$, $CONHSO_2R^9$, $CONR^{11}R^{12}$, $CONHNR^{11}R^{12}$, $CONHN^+R^{11}R^{12}R^{13}R^{14-}$, $CO_2^-R^{15}$ or $COON=CR^9R^{10}$;
R^6, R^9 and R^{10} are H or an optionally substituted alkyl, aryl, alkenyl or alkynyl group;
R^7, R^8, R^{11}, R^{12} and R^{13} are H or an optionally substituted alkyl, alkenyl, aryl or alkynyl group or any two of R^7, R^8, R^{11}, R^{12} and R^{13} together with the atom to which they are attached form a cycloalkyl or heterocyclic ring;
R^{14-} is an agriculturally acceptable anion; and
R^{15+} is an agriculturally acceptable cation.

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HETEROCYCLIC COMPOUNDS

The present invention relates to novel substituted indole derivatives, processes for their preparation, their use as herbicides and herbicidal compositions containing them.

European Patent No. 178,708 A describes certain benzheterocyclyl-phenyl ether derivatives which have herbicidal activity.

According to the present invention there is provided a compound of formula (I) in which Ar is an optionally substituted aryl or heterocyclic ring system;

W is O or NR^1 where R^1 is hydrogen or lower alkyl;

Y is a 5 membered saturated or unsaturated ring containing one nitrogen atom, the ring being substituted on at least one carbon or nitrogen atom by a group $CR^2R^3XR^4$ and optionally by one or more additional groups R^a, each R^a being independently selected from OH, optionally substituted alkoxy, halogen, optionally substituted alkyl, alkenyl or alkynyl, CO_2R^5, CN, oxo, $S(O)_pR^5$, where p is 0, 1 or 2; X is $(CH_2)_n$, CH=CH, $CH(OR^6)CH_2$, $COCH_2$; where n is 0, 1 or 2; R^2 and R^3 are independently selected from H, optionally substituted alkyl, alkenyl or alkynyl, halogen, NR^7R^8 or R^2 and R^3 together with the carbon to which they are attached form an optionally subitituted alkenyl or cycloalkyl group;

R^4 is CO_2R^9, CN, COR^9, CH_2OR^9, $CH(OH)R^9$, $CH(OR^9)R^{10}$, $CSNH_2$, $COSR^9$, $CSOR^9$, $CONHSO_2R^9$, $CONR^{11}R^{12}$, $CONHNR^{11}R^{12}$, $CONHN^+R^{11}R^{12}R^{13}R^{14-}$, $CO_2^-R^{15+}$ or $COON=CR^9R^{10}$;

R^5, R^6, R^9 and R^{10} are independently selected from H or an optionally substituted alkyl, aryl, alkenyl or alkynyl group;

R^7, R^8, R^{11}, R^{12} and R^{13} are independently selected from H or an optionally substituted alkyl, alkenyl, aryl or alkynyl group or any two of R^7, R^8, R^{11}, R^{12} and R^{13} together with the atom to which they are attached form a cycloalkyl or heterocyclic ring;

R^{14-} is an agriculturally acceptable anion; and

$R15^+$ is an agriculturally acceptable cation;

As used herein the term "alkyl" includes straight or branched chains containing up to 10 carbon atoms preferably from 1 to 6 carbon atoms. The term "lower" used in relation to alkyl, alkenyl or alkynyl groups means that the group contains up to 3 carbon atoms. The terms "alkenyl" and "alkynyl" refer to unsaturated straight or branched chains having from 2 to 10 and preferably from 2 to 6 carbon atoms. The term "cycloalkyl" includes rings containing from 3 to 9 carbon atoms, preferably from 3 to 6 carbon

atoms. The term "alkoxy" includes straight or branched chains containing up to 10 carbon atoms preferably from 1 to 6 carbon atoms.

The term "haloalkyl" and "haloalkoxy" refer to alkyl and alkoxy groups respectively substituted by at least one halogen atom such as fluorine, chlorine or bromine. A particular haloalkyl group is trifluoromethyl. The term "aryl" includes phenyl and naphthyl. The term "heterocyclic" includes rings of up to 10 atoms, preferably up to 6 atoms up to 3 of which are selected from oxygen, nitrogen or sulphur. The term halogen includes fluorine, chlorine, bromine and iodine.

A suitable aryl ring system is phenyl.

Suitable heterocyclic ring systems for Ar are rings of up to 10 atoms, up to 3 of which are selected from oxygen, nitrogen or sulphur, preferably aromatic rings such as pyridine and pyrazole.

Suitable optional substitutents for the aryl or heterocyclic ring systems Ar and aryl groups R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12} or R^{13} are up to 5 preferably up to 3 members selected from halogen (fluoro, chloro, bromo or iodo), lower alkyl, haloalkyl (for example CF_3), haloalkoxy (for example OCF_3), nitro, cyano, lower alkoxy (for example methoxy) or $S(O)mR^{16}$ where m is 0, 1 or 2 and R^{16} is alkyl (for example thiomethyl, sulphinylmethyl and sulphonylmethyl).

Examples of optional substituents for alkyl, alkenyl, alkynyl groups R^2, R^3, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12} and R^{13} and in ring Y, and alkoxy groups in ring Y include one or more groups selected from halo such as fluoro, chloro or bromo; nitro; nitrile; aryl such as phenyl; CO_2R^{17}, or $NHCH_2CO_2R^{17}$ wherein R^{17} is hydrogen, C_{1-6} alkyl or an agriculturally acceptable cation; $NHCOR^{18}$ where R^{18} is hydrogen or C_{1-6} alkyl; C_{1-6} alkoxy; oxo; $S(O)p\ R^{19}$ where p is 0, 1 or 2 and R^{19} is alkyl (for example thiomethyl, sulphinylmethyl and sulphonylmethyl); amino; mono- or di-C_{1-6} alkyl amino; $CONR^{20}R^{21}$ wherein R^{20} and R^{21} are independently selected from hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl or C_{2-6} alkynyl or R^{20} and R^{21} are joined together to form a heterocyclic ring having up to 7 ring atoms 3 of may be selected from oxygen, nitrogen or sulphur. An example of a heterocyclic substitutent is tetrahydrofuranyl.

Examples of agriculturally acceptable cations R^{15+} and R^{17} include sodium, potassium or calcium ions, sulphonium or sulphoxonium ions such as those of formula $S(O)_qR^{11}R^{12}R^{13}$ where q is 0 or 1, or ammonium or tertiary ammonium ions of formula $N^+R^{11}R^{12}E^{13}R^{22}$ where R^{11}, R^{12} and R^{13} are as herein before defined and R^{22} is a group as defined for R^{11}.

Suitable substituents for alkyl, alkenyl or alkynyl groups in these cation R^{11}, R^{12}, R^{13} and R^{22} include hydroxy and aryl. Suitably where any of R^{11}, R^{12}, R^{13} and R^{22} are optionally substituted alkyl, they contain from 1 to 4 carbon atoms.

Particular examples of R^{11}, R^{12}, R^{13} and R^{22}, in these cations are hydrogen, ethyl, isopropyl, 2-hydroxyethyl and benzyl.

Examples of agriculturally acceptable anions R^{14-} include halide ions such as iodide.

Suitable halo groups R^2 and R^3 include fluorine, chlorine and bromine.

Suitable heterocyclic rings formed from two of R^7, R^8, R^{11}, R^{12} and R^{13} and the atom to which they are attached are pyrrolidine, piperidine and morpholine.

Suitable rings formed by Y and the ring to which it is fused include groups of formula (ii) and (iii) wherein R^b and R^c are independently selected from H or a group R^a where R^a, R^2, R^3, R^4 and X are as hereinbefore defined.

Preferably R^2 is H.

Preferably R^3 is H or is C_{1-3} alkyl, in particular methyl.

Preferably R^4 is CN or CO_2R^9, most preferably CO_2R^9.

A preferred example of R^9 is optionally substituted C_{1-6} alkyl, especially ethyl.

Preferred groups Ar are groups of sub-formula (i).

where R^{23} is hydrogen or halo;

J is N or CR^{24} where R^{24} is halo or nitro.

Preferably J is a group CR^{24}.

Suitably halo groups for R^{23} and R^{24} are fluorine and chlorine. Most preferably one of R^{23} or R^{24} is fluorine and the other is chlorine.

Ar is preferably optionally substituted phenyl.

W is preferably oxygen.

Preferably X is $(CH_2)n$ where n is zero or 1, especially zero.

The formula (I) given above is intended to include tautomeric forms of the structure drawn, as well as physically distinguishable modifications of the compounds which may arise, for example, from different ways in which the molecules are arranged in a crystal lattice, or from the inability of parts of the molecule to rotate freely in relation to other parts, or from geometrical isomerism, or from intra-molelcular or inter-molecular hydrogen bonding, or otherwise.

Some of the compounds of the invention can exist in enantiomeric forms. The invention includes both individual enantiomers and mixtures of the two in all proportions.

Particular examples of compounds according to the invention are listed in Tables I to III.

TABLE I

The compounds in this Table are of general formula (IA)

Compound No.	R^{30}	R^{31}	R^{32}	R^{33}	R^{34}	R^{35}	Characterising Data
1	H	CH_2CN	H	CF_3	C-F	Cl	mp 166-169°C
2	H	CH2CO_2H	H	CF_3	C-F	Cl	mp 155-158°C
3	H	$CH_2CO_2CH_3$	H	CF_3	C-F	Cl	mp 83-85°C
4	H	$CH_2CO_2C_2H_5$	H	CF_3	C-F	Cl	mp 117-118°C
5	CH_3	CH_2CO_2H	H	CF_3	C-F	Cl	mp 146-148°C
6	CH_3	$CH_2CO_2CH_3$	H	CF_3	C-F	Cl	gum ^1H NMR δH ($CDCl_3$): 7.6(s)1H; 7.4(dd)1H; 7.25(d)1H; 7.05(d)1H; 6.95(dd)1H; 3.75(s)3H; 3.7(s)2H; 3.65(s)3H.
7	CH_3	$CH_2CO_2C_2H_5$	H	CF_3	C-F	Cl	mp 92-94°C

TABLE 1 (continued)

Compound No.	R^{30}	R^{31}	R^{32}	R^{33}	R^{34}	R^{35}	Characterising Data
8	$CH_2CH=CH_2$	CH_2COOH	H	CF_3	C-F	Cl	7.6(s)1H; 7.35(dd)1H; 7.25(d)1H; 7.15(d)1H; 7.1(d)1H; 6.9(dd)1H; 6.0(m)1H; 5.2(q)2H; 4.7(d)2H; 3.7(s)2H.
9	C_2H_5	$CH_2COOC_2H_5$	H	CF_3	C-F	Cl	7.6(s)1H; 7.35(d)1H; 7.25(d)1H; 7.15(d)1H; 7.05(d)1H; 6.95(dd)1H; 4.1(m)4H; 3.65(s)2H; 1.45(t)3H; 1.2(t)3H.

TABLE II

The compounds in this Table are of general formula (IB)

Compound No.	R^{36}	R^{37}	R^{38}	R^{33}	R^{34}	R^{35}	Characterising Data
10	H	$CH(CH_3)CO_2H$	H	CF_3	C-F	Cl	mp 127-129°C
11	H	$CH(CH_3)CO_2C_2H_5$	H	CF_3	C-F	Cl	oil ^{1}H NMR δH ($CDCl_3$): 7.6(s)1H; 7.55(d)1H; 7.4(d)1H; 7.25(d)1H; 6.9(s)1H; 6.75(dd)1H; 6.55(d)1H; 5.0(q)1H; 4.15(q)2H; 1.8(d)3H; 1.2(t)3H.

TABLE II (continued)

Compound No.	R^{36}	R^{37}	R^{38}	R^{33}	R^{34}	R^{35}	Characterising Data
12	Cl	$CH(CH_3)CO_2C_2H_5$	H	CF_3	C-F	Cl	oil ^1H NMR δH ($CDCl_3$): 7.6(s)1H; 7.5(d)1H; 7.4(dd)1H; 7.2(s)1H; 6.85(s)1H; 6.8(d)1H; 4.95(q)1H; 4.15(q)1H; 1.75(d)3H; 1.2(t)3H.
13	H	$CH(CH_3)CO_2C_2H_5$	H	CF_3	C-H	Cl	oil 1H NMR δH $CDCl_3$ 7.7(d)1H; 7.6(d)1H; 7.35(dd)1H; 7.3(d)1H; 7.05(d)1H;6.85(m)2H; 6.6(d)1H; 5.0(q)1H; 4.2(q)CH; 1.8(d)3H; 1.2(t)3H.
14	Cl	$CH(CH_3)CO_2C_2H_5$	Cl	CF_3	C-H	Cl	oil 1H NMR δH $CDCl_3$ 7.75(d)1H; 7.6(d)1H; 7.4(dd)1H; 7.0(d)1H; 6.95(dd)1H; 6.85(d)1H; 5.3(q)1H; 4.2(q)2H; 1.8(d)3H; 1.2(t)3H.

TABLE II (continued)

Compound No.	R^{30}	R^{31}	R^{32}	R^{33}	R^{34}	R^{35}	Characterising Data
15	Cl	$CH(CH_3)CO_2C_2H_5$	H	CF_3	C-H	Cl	7.75(d)1H; 7.6(d)1H; 7.4(dd)1H; 7.3(s)1H; 7.05(d)1H; 6.95(dd)1H; 6.85(d)1H; 5.0(q)1H; 4.2(q)2H; 1.8(d)3H; 1.2(t)3H.
16	CN	$CH(CH_3)CO_2C_2H_5$	CF_3	CF_3	C-F	Cl	7.8(d)1H; 7.6(s)1H; 7.45(dd)1H; 7.0(dd)1H; 6.9(d)1H; 5.2(q)1H; 4.15(q)2H; 1.8(d)3H; 1.1(t)3H.
17	CN	$CH(CH_3)CO_2C_2H_5$	CF_3	CF_3	C-H	Cl	7.9(d)1H; 7.8(d)1H; 7.5(dd)1H; 7.1(dd)1H; 7.05(d)1H; 7.0(d)1H; 5.25(q)1H; 4.2(q)2H; 1.8(d)3H; 1.15(t)3H.
18	CN	$CH(CH_3)CO_2H$	CF_3	CF_3	C-F	Cl	8.0(d)2H; 7.7(d)1H; 7.3(s)1H; 6.9(d)1H; 4.8(b)1H; 1.5(d)3H.
19	Cl	$CH(CH_3)CO_2H$	H	CF_3	C-H	Cl	m.pt 137°C
20	CN	$CH(CH_3)CO_2H$	CF_3	CF_3	C-H	Cl	8.15(s)1H; 7.95(d)1H; 7.75(dd)1H; 7.5(s)1H; 7.3(dd)1H; 7.2(d)1H; 5.8-5.6(t)1H; 3.7-3(t)1H; 1.7(d)3H.

TABLE II (continued)

Compound No.	R^{30}	R^{31}	R^{32}	R^{33}	R^{34}	R^{35}	Characterising Data
21	CN	$CH(CH_3)CO_2C_2H_5$	H	CF_3	C-H	Cl	7.82(s)1H; 7.8(d)1H; 7.75(d)1H; 7.4(dd)1H; 7.05(d)1H; 7.02(dd)1H; 6.9(d)1H; 5.05(q)1H; 4.2(q)2H; 1.85(d)3H; 1.2(t)3H.
22	CN	$CH(CH_3)CO_2C_2H_5$	H	CF_3	C-F	Cl	m.pt 132-134°C
23	CN	$CH(CH_3CO_2C_2H_5$	Cl	CF_3	C-F	Cl	7.65(s)1H; 7.6(d)1H; 7.4(d)1H; 6.9(s)1H; 6.85(d)1H; 5.3(q)1H; 4.2(q)2H; 1.8(d)3H; 1.2(t)3H.

TABLE III

The compound in this Table is of general formula (IC)

Compound No.	R^{39}	R^{33}	R^{34}	R^{35}	Characterising Data
24	$CH(CH_3)CO_2C_2H_5$	CF_3	C-F	Cl	oil δH ($CDCl_3$): 7.55(s)1H; 7.35(dd)1H; 6.9(d)1H; 6.05(s)1H; 6.0(d)1H; 4.15(m)3H; 3.6(m)2H; 2.9(m)2H; 1.45(d)3H; 1.2(t)3H.

Compounds of formula (I) can be prepared from compounds of formula (II) where Ar and W are as defined in relation to formula (I) and Y′ is as defined for Y in formula (I) except that it carries no group $CR^2R^3XR^4$ by reaction with a compound of formula (III) wherein X, R^2, R^3 and R^4 are as

defined in relation to formula (I) and Z is a leaving group, optionally in the presence of a base.

Suitable leaving groups Z include halogen, such as fluorine, bromine and chlorine, and sulphonates such as methanesulphonate and p-toluenesulphonate.

Suitable bases for use in the reaction include bases such as sodium hydride, and alkali metal carbonates and hydroxides.

The reaction is preferably carried out in an organic solvent such as dimethylformamide, dimethylsulphoxide, a lower alkanol, or a lower ketone. Moderate temperatures, for example of from 20° to 90°C are suitably employed. Conveniently the reaction is carried out at 25° to 30°C.

Compounds of formula (II) can be prepared by reacting a compound of formula (IV) where W is as defined in relation to formula (I) and Y′ is as defined in relation to formula (II) with a compound of formula (V) wherein Ar is as defined in relation to formula (I) and Z′ is a leaving group, optionally in the presence of a base to form an aryl ether, followed by modification of the phenol substituents to give the desired indole.

Suitable leaving groups Z′ include halogen, such as fluorine, bromine and chlorine.

Suitable bases for use in the reaction include bases such as sodium hydride, and alkali metal carbonates and the reaction is preferably carried out in an organic solvent such as dimethylformamide, dimethylsulphoxide, a lower alkanol, or a lower ketone. Moderate temperatures, for example from 20° to 90°C are suitably employed. Conveniently the reaction is carried out at 25° to 30°C.

Alternatively compounds of formula (I) may be prepared from compounds of formula (VI) where W and Y are as defined in relation to formula (I) by reaction with compounds of formula (V) as hereinbefore defined using conditions described for the preparation of compounds of formula (II). Compounds of formulae (II) and (VI) are known compounds or may be made by known methods from known compounds. For example compounds of formula (VI) can be prepared as shown in Scheme 1.

The indole of formula (ii) may also be reduced to an indoline of formula (iv) by known methods to produce the corresponding compounds of formula (I).

If desired one or more of the following steps may be carried out:

i) when R^4 is alkoxycarbonyl hydrolysing to the corresponding

acid;

ii) when R^4 is CN, converting it to an acid group;

iii) when R^4 is COOH esterifying or forming a salt; amide, sulphonamide, hydrazide or hydrazinium derivative;

iv) when R^4 is an alcohol, oxidation to the corresponding acid or aldehyde;

v) when R^4 is alkoxycarbonyl, reduction to an alcohol;

vi) when R^4 is an amide, dehydration to the corresponding nitrile;

vii) conversion of an N-H group to N-alkyl groups by alkylation under basic conditions; and

(viii) conversion of an indole group formed by Y to its dihydro derivative by reduction under standard conditions;

The compounds of formula (I) are active as herbicides and therefore, in a further aspect the invention provides a process for severely damaging or killing unwanted plants which process comprises applying to the plants, or to the growth medium of the plants, an effective amount of a compound of formula (I) as hereinbefore defined.

The compounds of formula (I) are active against a broad range of weed species including monocotyledenous and dicotyledonous species. They may show some selectivity towards certain species; they may be used as selective herbicides in rice and wheat crops.

The compounds of formula (I) may be applied directly to the plant (post-emergence application) or to the soil before the emergence of the plant (pre-emergence application). They are particularly useful when applied post-emergence.

The compounds of formula (I) may be used on their own to inhibit the growth of, severely damage, or kill plants but are preferbly used in the form of a composition comprising a compound of the invention in admixture with a carrier comprising a solid or liquid diluent.

Therefore, in yet a further aspect, the invention provides plant growth inhibiting, plant damaging, or plant killing compositions comprising a compound of formula (I) as hereinbefore defined and an inert carrier or diluent.

Compositions containing compounds of formula (I) include both dilute compositions, which are ready for immediate use, and concentrated compositions, which require to be diluted before use, usually with water. Preferably the compositions contain from 0.01% to 90% by weight of the active ingredient. Dilute compositions ready for use preferably contain

from 0.01% to 2% of active ingredient, while concentrated compositions may contain from 20% to 90% of active ingredient, although from 20% to 70% is usually preferred.

The solid compositions may be in the form of granules, or dusting powders wherein the active ingredient is mixed with a finely divided solid diluent, e.g. kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, Fuller's earth and gypsum. They may also be in the form of dispersible powders or grains, comprising a wetting agent to facilitate the dispersion of the powder or grains in liquid. Solid compositions in the form of a powder may be applied as foliar dusts.

Liquid compositions may comprise a solution or dispersion of an active ingredient in water optionally containing a surface-active agent, or may comprise a solution or dispersion of an active ingredient in a water-immiscible organic solvent which is dispersed as droplets in water.

Surface-active agents may be of the cationic, anionic, or non-ionic type or mixtures thereof. The cationic agents are, for example, quaternary ammonium compounds (e.g. cetyltrimethylammonium bromide). Suitable anionic agents are soaps; salts of aliphatic mono esters of sulphuric acid, for example sodium lauryl sulphate; and salts of sulphonated aromatic compounds, for example sodium dodecylbenzenesulphonate, sodium, calcium, and ammonium lignosulphonate, butylnaphthalene sulphonate, and a mixture of the sodium salts of diisopropyl and triisopropylnaphthalenesulphonic aid. Suitable non-ionic agents are the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl alcohol, or with alkylphenols such as octyl- or nonyl-phenol (e.g. Agral 90) or octyl-cresol. Other non-ionic agents are the partial esters derived from long chain fatty cids and hexitol anhydrides, for example sorbitan monolaurate; the condensation products of the partial ester with ethylene oxide; and the lecithins; silicone surface active agents (water soluble surface active agents having a skeleton which comprises a siloxane chain e.g. Silwet L77). A suitable mixture in mineral oil is Atplus 411F.

The aqueous solutions or dispersions may be prepared by dissolving the active ingredient in water or an organic solvent optionally containing wetting or dispersing agent(s) and then, when organic solvents are used, adding the mixture so obtained to water optionally containing wetting or dispersing agent(s). Suitable organic solvents include, for example, ethylene di-chloride, isopropyl alcohol, propylene glycol, diacetone

alcohol, toluene, kerosene, methylnaphthalene, the xylenes and trichloroethylene.

The compositions for use in the form of aqueous solutions or dispersions are generally supplied in the form of a conentrate containing a high proportion of the active ingredient, and the concentrate is then diluted with water before use. The concentrates are usually required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water to form aqueous preparations which remain homogenous for a sufficient time to enable them to be applied by conventional spray equipment. Concentrates conveniently contain 20-90%, preferably 20-70%, by weight of the active ingredient(s). Dilute preparations ready for use may contain varying amounts of the active ingredients(s) depending upon the intended purpose; amounts of 0.01% to 10.0% and preferably 0.1% to 2%, by weight of active ingredient(s) are normally used.

A preferred form of concentrated composition comprises the active ingredient which has been finely divided and which has been dispersed in water in the presence of a surface-active agent and a suspending agent. Suitable suspending agents are hydrophilic colloids and include, for example, polyvinylpyrrolidone and sodium carboxymethylcellulose, and the vegetable gums, for example gum acacia and gum tragacanth. Preferred suspending agents are those which impart thixotropic properties to, and increase the viscosity of the concentrate. Examples of preferred suspending agents include hydrated colloidal mineral silicates, such as montmorillonite, beidellite, nontronite, hectorite, saponite, and suacorite. Bentonite is especially preferred. Other suspending agents include cellulose derivatives and polyvinyl alcohol.

The rate of application of the compounds of the invention will depend on a number of factors including, for example, the compound chosen for use, the identity of the plants whose growth is to be inhibited, the formulations selected for use and whether the compound is to be applied for foliage or root uptake. As a general guide, however, an application rate of from 0.01 to 20 kilograms per hectare is suitable while from 0.025 to 10 kilograms per hectare may be preferred.

The compositions of the invention may comprise, in addition to one or more compounds of the invention, one or more compounds not of the invention but which possess biological activity. Accordingly in yet a still further embodiment the invention provides a herbicidal composition comprising a

mixture of at least one herbicidal compound of formula (I) as hereinbefore defined with at least one other herbicide.

The other herbicide may be any herbicide not having the formula (I). It will generally be a herbicide having complementary action in the particular application.

Examples of useful complementary herbicides include:

A. benzo-2,1,3-thiadiazin-4-one-2,2-dioxides such as bentazone;

B. hormone herbicides, particularly the phenoxy alkanoic acids such as MCPA, MCPA-thioethyl, dichlorprop, 2,4,5-T, MCPB, 2,4-D, 2,4-DB, mecoprop, trichlopyr, clopyralid, and their derivatives (eg. salts, esters and amides);

C. 1,3 dimethylpyrazole derivatives such as pyrazoxyfen, pyrazolate and benzofenap;

D. Dinitrophenols and their derivatives (eg. acetates) such as dinoterb, dinoseb and its ester, dinoseb acetate;

E. dinitroaniline herbicides such as dinitramine, trifluralin, ethalflurolin, pendimethalin, oryzalin;

F. arylurea herbicides such as diuron, flumeturon, metoxuron, neburon, isoproturon, chlorotoluron, chloroxuron, linuron, monolinuron, chlorobromuron, daimuron, methabenzthiazuron;

G. phenylcarbamoyloxyphenylcarbamates such as phenmedipham and desmedipham;

H. 2-phenylpyridazin-3-ones such as chloridazon and norflurazon;

I. uracil herbicides such as lenacil, bromacil and terbacil;

J. triazine herbicides such as atrazine, simazine, aziprotryne, cyanazine, prometryn, dimethametryn, simetryne, and terbutryn;

K. phosphorothioate herbicides such as piperophos, bensulide, and butamifos;

L. thiolcarbamate herbicides such as cycloate, vernolate, molinate, thiobencarb, butylate*, EPTC*, tri-allate, di-allate, esprocarb, tiocarbazil, pyridate, and dimepiperate;

M. 1,2,4-triazin-5-one herbicides such as metamitron and metribuzin;

N. benzoic acid herbicides such as 2,3,6-TBA, dicamba and chloramben;

O. anilide herbicides such as pretilachlor, butachlor, alachlor, propachlor, propanil, metazachlor, metolachlor, acetochlor, and dimethachlor;

P. dihalobenzonitrile herbicides such as dichlobenil, bromoxynil and ioxynil;

Q. haloalkanoic herbicides such as dalapon, TCA and salts thereof;

R. diphenylether herbicides such as lactofen, fluroglycofen or salts or ester thereof, nitrofen, bifenox, aciflurofen and salts and esters thereof, oxyfluorfen, fomesafen, chlornitrofen and chlomethoxyfen;

S. phenoxyphenoxypropionate herbicides such as diclofop and esters thereof such as the methyl ester, fluazifop and esters thereof, haloxyfop and esters thereof, quizalofop and esters thereof and fenoxaprop and esters thereof such as the ethyl ester;

T. cyclohexanedione herbicides such as alloxydim and salts thereof, sethoxydim, cycloxyidim, tralkoxydim, and clethodim;

U. sulfonyl urea herbicides such as chlorosulfuron, sulfometuron, metsulfuron and esters thereof; benzsulfuron and esters thereof such as DPX-M6313, chlorimuron and esters such as the ethyl ester thereof pirimisulfuron and esters such as the methyl ester thereof, 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-zyl)-3-methylureidosulphonyl) benzoic acid esters such as the methyl ester thereof (DPX-LS300) and pyrazosulfuron;

V. imidazolidinone herbicides such as imazaquin, imazamethabenz, imazapyr and isopropylammonium salts thereof, imazethapyr;

W. arylanilide herbicides such as flamprop and esters thereof, benzoylprop-ethyl, diflufenican;

X. amino acid herbicides such as glyphosate and glufosinate and their salts and esters, sulphosate and bialaphos;

Y. organoarsenical herbicides such as monosodium methanearsonate (MSMA);

Z. herbicidal amide derivative such as napropamide, propyzamide, carbetamide, tebutam, bromobutide, isoxaben, naproanilide and naptalam;

AA. miscellaneous herbicides including ethofumesate, cinmethylin, difenzoquat and salts thereof such as the methyl sulphate salt, clomazone, oxadiazon, bromofenoxim, barban, tridiphane, flurochloridone, quinchlorac, dithiopyr and mefanacet;

BB. Examples of useful contact herbicides include:
bipyridylium herbicides such as those in whichthe active entity is paraquat and those in which the active entity is diquat;

* These compounds are preferably employed in combination with a safener such as dichlormid.

The following Examples illustrate the invention :

EXAMPLE 1

This Example illustrates the preparation of compound 1 in Table 1:

Step A

3-cyanomethyl-5-hydroxy-1H-indole (1.0g, 5.8mmol) and 5-chloro-3,4-difluorobenztrifluroide (1.26g, 5.8mmol) were dissolved in dimethylsulphoxide (25cm^3) and the potassium carbonate (1.6g, 12mmol) added. The mixture was stirred and heated at 100°C for 2.5 hours. The mixture was cooled and poured into water and extracted twice with dimethyl sulphoxide. The resulting solution was washed with brine and dried ($MgSO_4$). The solvent was evaporated leaving a black oil which was purified by flash chromatography on silica gel using ether/hexane 1:1 as eluent. Compound 1, 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxy-3-cyanomethyl-1H-indole was obtained as a white solid.

EXAMPLE 2

This Example describes the preparation of compound 4 in Table I.

Step A

5-hydroxyindole-3-acetic acid (1.9g, 10mmol) was dissolved in ethanol (50cm^3) and concentrated sulphuric acid (1.5cm^3) added with stirring. The mixture was stirred and refluxed for 3 hours, cooled, excess ethanol evaporated off, and the residue dissolved in diethyl ether. The ether solution was washed with water, saturated sodium bicarbonate solution and dried. The solvent was evaporated leaving ethyl 5-hydroxyindole-3-acetate as a light brown oil. (1.71g).

Step B

The ester obtained in step A (1.25g, 5.7mmol) and 5-chloro-3,4-difluorobenzotrifluoride were dissolved in dimethyl sulphoxide (30cm^3) and potassium carbonate (0.83g, 16mmol) added. The mixture was stirred at room temperature. After 24 hours the mixture was poured into water and extracted twice with ethyl acetate. The combined extracts were washed with water and brine and dried (mgS04). The solvent was evaporated leaving a black oil which was purified by flash chromatography on silica gel using ether/hexane 1:1 as eluent. Compound 4 ethyl 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxy-indole-3-acetate (0.31g) was obtained as a colourless solid. m.p. 117-119°C.

EXAMPLE 3

This Example describes the preparation of compound 7 in Table I.

Sodium hydride (0.013g, 3.1mmol) was suspended in dimethylformamide ($10cm^3$). A solution of compound 4 (1.3g, 3.1mmol) in dimethylformamide ($10cm^3$) was added dropwise with stirring at room temperature. After addition the mixture was stirred at room temperature for ¼ hour and then methyl iodide (0.5g, 3.5mmol) was added. The mixture was stirred for 3 hours at room temperature, poured into water and extracted twice with ethyl acetate. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was evaporated and the product purified by flash chromatography on silica gel using ether/hexane 1:1 as eluent to give compound 7, ethyl 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxy-1-methylindole-3-acetate (0.62g) as a colourless solid m.p. 92-94°. Compound No. 9 was prepared in an analogous manner using appropriate reactants.

EXAMPLE 4

This Example illlustrates the preparation of compound 2 in Table I. Compound 4, ethyl 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxy-indole-3-acetate (3.0g, 7.2mmol) was dissolved in isopropanol ($40cm^3$) and a solution of sodium hydroxide (0.3g, 8mmol) in water ($10cm^3$) added. The mixture was heated under reflux for 3½ hours, cooled and concentrated in vacuo. The residue was partitioned between dilute aqueous hydrochloric acid and ethyl acetate and the organic extracts were combined, washed with water, dried ($MgSO_4$) and evaporated under reduced pressure to give compound 2, 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxyindole-3-acetic acid (2.3g) as a colourless solid m.p. 155-158°.

Compounds 5 and 8 in Table I and compounds 10 and 20 in Table II were prepared by analogous processes using appropriate reactants.

EXAMPLE 5

This Example illustrates the preparation of compound 3 in Table I.

A few drops of concentrated sulphonic acid were added to a solution of compound 4, 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxyindole-3-acetic acid (0.5g, 1.3mmol) in methanol ($20cm^3$) and the mixture was heated under reflux for 3½ hours. The mixture was cooled, poured into water and extracted with ethyl acetate. The organic extracts were combined, washed successively with saturated aqueous sodium bicarbonate solution and water, dried ($MgSO_4$) and evaporated in vacuo to give compound 5, methyl 5-(2-chloro-6-fluoro-4-trifluoromethyl)phenoxyindole-3-acetate (0.4g) as a colourless solid m.p. 83-85°. Compound 6 in Table I was prepared by an

analogous process using appropriate reactants.

EXAMPLE 6

This Example illustrates the preparation of compound 11 in Table II.

Step A (i)

Sodium hydride (0.55g, 23mmol) was suspended in dimethylformamide ($20cm^3$) and a solution of 6-methoxyindole (3.4g, 23mmol) in dimethylformamide ($25cm^3$) was added dropwise. After the addition was complete the reaction mixture was stirred at room temperature for 15 minutes, and then a solution of ethyl 2-bromopropionate (4.16g, 23mmol) in dimethylformamide ($20cm^3$) was added dropwise. The reaction mixtue was stirred at room temperature for 2 hours, poured into water and extracted with ethyl acetate. The organic extracts were combined, dried ($MgSO_4$) and evaporated in vacuo. The residue was further purified by flash column chromatography on silica gel, eluting with diethyl ether hexane 1:4 to give ethyl 2-(6-methoxyindol-1-yl)propionate (3.2g) as an oil. δH ($CDCl_3$): 7.15(d)1H; 7.5(d)1H; 6.8(d)2H; 6.5(d)1H; 5.05(q)1H; 4.15(q)2H; 3.85(s)3H; 1.8(d)3H; 1.2(t)3H. Ethyl 2-(6-ethoxyindol-1-yl)propionate may also be employed as a starting materal and this was prepared by an analogous process using appropriate reactants.

Step A(ii)

Sodium cyanoborohydride (1.6g, 26mmol) was added portionwise to a solution of 2-(6-ethoxyindol-1-yl)propionate (1.7g, 6.6mmol) in acetic acid ($30cm^3$). After the addition was complete the reaction mixture was stirred at room temperature for 2 hours, poured into water and extracted with ethyl acetate. The organic extracts were combined, washed sucessively with saturated aqueous sodium bicaronate solution and water, dried ($MgSO_4$) and the solvent evaporated in vacuo to give ethyl 2-(6-ethoxyindolin-1-yl)-propionate (1.7g) as an oil. δH 6.9(d)1H; 6.2(dd)1H; 6.0(s)1H; 4.2(q)1H; 4.15(q)2H; 3.95(q)2H; 3.6(m)2H; 2.9(m)2H; 1.5(d)3H; 1.4(t)3H; 1.2(t)3H.

Step B

A solution of ethyl 2-(6-methoxyindol-1-yl)priopinate (1.9g, 7.6mmol) in dichloromethane ($30cm^3$) was cooled to below -70° in a dry ice/ acetone bath. Boron tribromide (2.9ml, 30mmol) was added dropwise at such a rate that the temperature of the mixture was maintained below -70° and once the addition was complete the mixture was stirred for 15 minutes and then allowed to warm to room temperature over a period of 3 hours. The mixture was then cooled in an ice bath and ethanol ($20cm^3$) was added. The mixture was stirred for 15 minutes and the solvent evaported under reduced

pressure. The residue was taken up in ethanol ($20cm^3$), a few drops of concentrated sulphuric acid added and the solution heated under reflux for 2 hours. The solvent was evaporated and the residue taken up in diethyl ether, washed successively with saturated aqueous sodium bicarbonate solution and water, dried (MgSO4) and evaporated in vacuo to give ethyl 2-(6-hydroxyindol-1-yl)propionate (1.8g) as an oil, used without further purification in the next step.

Step C

The ester (1.8g) obtained in step B, 3-chloro-4,5-difluoro-benzotrifluoride (1.7g, 8mmol) and potassium carbonate (1.2g, 9mmol) were heated together in dimethylsulphoxide ($25cm^3$) at 100°C for 3 hours. The mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The organic extracts were combined, washed with brine, dried ($MgSO_4$) and evaporated in vacuo. The resiude was further purified by flash column chromatography on silica gel eluting with diethyl ether/hexane 1:9 to give compound 9, ethyl 2-(6-[2-chloro-6-fluoro-4-trifluoromethyl]-phenoxyindol-1-yl)propionate (1.9g) as an oil.

Compounds 13, 21 and 22 in Table II and compound 24 in Table III were prepared by analogous processes using appropriate reactants.

EXAMPLE 7

This Example illustrates the preparation of compound 12 in Table II.

Compound 11, ethyl 2-(6-[2-chloro-6-fluoro-4-trifluoromethyl])-phenoxyindol-1-yl)propionate (0.5g, 1.2mmol) was dissolved in diethyl ether ($20cm^3$) and the solution was cooled in an ice bath. A solution of sulphuryl chloride (0.16g, 1.2mmol) in diethyl ether ($5cm^3$) was added dropwise and the reactions mixture was allowed to warm to room temperature over 2 hours. The mixture was washed with water, dried ($MgSO_4$) and the solvent evaported in vacuo. The residue was further purified by preparative thin layer chromatography on silica gel, eluting with diethyl ether/hexane 1:9 to give compound 12, ethyl 2-(3-chloro-6-[2-chloro-6-fluoro-4-tri-fluoromethyl)phenoxyindol-1-yl)propionate (0.25g) as an oil. Compound No. 23 was prepared in an analogous manner using appropriate reactants.

EXAMPLE 8

This Example illustrates the preparation of 3-cyano-6-methoxyindole.

Step A

A solution of 2-nitro-4-methoxyphenylacetonitrile (10.0g, 52mmol), dimethylformamide dimethylacetal ($13.8cm^3$, 104mmol) and pyrrolidine

($4.3cm^3$, 52mmol) in N,N-dimethylformamide ($80cm^3$) was heated to 100 °C for 16 hours. The mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The organic extracts were combined, washed with brine, dried ($MgSO_4$), filtered and the filtrate evaporated in vacuo to give an oily solid (10.35g) using immediately in Step B.

Step B

A solution of the product from Step A (10.35g) in toluene ($35cm^3$) and acetic acid ($20cm^3$) was added dropwise to a vigorously stirred mixture of iron powder (31g) and silica gel 230-400 mesh (61g) in toluene ($270cm^3$) and acetic acid ($80cm^3$) and once the addition was complete the mixture was heated to 100°C for 1 hour. The mixture was cooled to room temperature and filtered through a plug of silica gel (Kieselgel 60, finer than 230 mesh). The filtrate was evaporated in vacuo and the residue further purified by flash column chromatography on silica gel, eluting with dichloromethane to give 3-cyano-6-methoxyindole (1.1g) as a brown solid m.pt 174-176°C.

EXAMPLE 9

This Example illustrates the preparation of Compound No. 16 in Table II.

Step A

Sodium hydride (19.2g, 0.8mol) was suspended in N,N-dimethylformamide ($300cm^3$) and a solution of ethyl cyanoacetate (85.1 cm^3, 0.8mol) in N,N--dimethylformamide ($300cm^3$) was added dropwise. Once the addition was complete the reaction mixture was stirred at room temperature for 15 minutes, and then a solution of 4-chloro-3-nitroanisole (75.2g 0.4mol) in N,N-dimethylformamide ($300cm^3$) was added, together with caesium fluoride (1.0g, 6.6mmol). After the addition was complete the reaction mixture was stirred at between 60 and 70°C for 24 hours, then cooled to room temperature, poured into water, the solution acidified, and extracted with ethyl acetate. The organic extracts were combined, washed sequentially with water and brine ($MgSO_4$) and filtered. The filtrate was evaporated in vacuo and the residue purified by flash column chromatography on silica gel, eluting with diethyl ether:hexane 1:1 to give ethyl 2-cyano-2-(2--nitro-4-methoxyphenyl)acetate (76.0g) as an oil.

Step B

The cyanoacetate (76.0g, 0.29mol) obtained in Step A above was stirred in saturated aqueous sodium carbonate solution ($1000cm^3$) at 55°C for 22 hours. The mixture was cooled, extracted with ethyl acetate and the

organic extracts were combined, washed with water, dried ($MgSO_4$), filtered and the filtrate evaporated to give a solid. Trituration with diethyl ether gave 2-nitro-4-methoxyphenylacetonitrile (45.7g) as a yellow solid m.pt 69-71°C.

Step C

Iron filings (53.8g, 0.96mol) were added to a vigorously stirred solution of 2-nitro-4-methoxyphenylacetonitrile (45.7g, 0.24mol) in isopropanol (800cm^3) and water (276cm^3). Concentrated hydrochloric acid (49.6cm^3) was added portionwise, and once the addition was complete the mixture was stirred and heated under reflux for 2½ hours. The mixture was cooled to room temperature and filtered. The filtrate was concentrated in vacuo, and then extracted with ethyl acetate. The organic extracts were combined, washed with water, dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was triturated with diethyl ether to give 2-amino--methoxyphenylacetonitrile (21.0g) as a pale brown solid. ^1H NMR ($CDCl_3$): 7.1(d)1H; 6.4(dd)1H; 6.3(d)1H; 3.7(bs)1H; 3.75(s)3H; 3.5(s)2H.

Step D

Trifluoroacetic anhydride (13.4g, 64mmol) in tetrahydrofuran (30cm^3) was added dropwise to a solution of 2-nitro-4-methoxyphenylacetonitrile (10.3g, 64mmol) and diisopropylethylamine (8.8g, 68mmol) in tetrahydrofuran (130cm^3) and the mixture was stirred at room temperature for 3 hours. The mixture was poured into water and extracted with ethyl acetate. The organic extracts were combined, washed with water, dried ($MgSO_4$), filtered and the filtrate evaporated in vacuo. Trituration with diethyl ether gave 4-methoxy-2-N-trifluoroacetamidophenylacetonitrile (12.5g) as a light browb solid. m.pt 120-121°C.

Step E

A solution of 4-methoxy-2-N-trifluoroacetamidophenylacetonitrile (12.4g, 48mmol) in tetrahydrofuran (100cm^3) was added dropwise to a suspension of sodium hydride (1.15g, 48mmol) in tetrahydrofuran (100cm^3) at 0°C and the mixture stirred until effervescence had ceased. The mixture was allowed to warm to room temperature and trimethylsilyl chloride (5.21g, 48mmol) was added. The mixture was stirred at room temperature for 45 minutes, potassium t-butoxide (10.75g, 96mmol) was added and the mixture heated to reflux for 2 hours. The mixture was cooled to room temperature, poured into saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic extracts were dried ($MgSO_4$), filtered and the filtrate evaporated in vacuo. The residue was further purified by flash

column chromatography on silica gel, eluting with dichloromethane to give 3-cyano-6-methoxy-2-trifluoromethyl indole (4.90g) as a grey solid m.pt 121-124°C.

Step F

A solution of the indole (4.89g, 20.4mmol) in N,N-dimethylformamide ($35cm^3$) was added to a suspension of sodium hydride (0.49g, 20.4mmol) in N,N-dimethylformamide ($15cm^3$) and once the addition was complete the mixture was heated at 70°C for 15 minutes, and then cooled to 40°C. A solution of ethyl 2-bromopropionate (3.69g, 20.4 mmol) in N,N-dimethyl--formamide ($5cm^3$) was added portionwise, and the mixture stirred at 70°C for 20 hours. A further quantity of sodium hydride (0.49g, 20,4 mmol) and ethyl 2-bromoproponate (1.85g, 10.2 mmol) were added and the mixture stirred at 70°C for a further 2 hours.

The mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The organic extracts were combined, washed with water, dried ($MgSO_4$) and filtered. The filtrate was evaporated in vacuo and the residue further purified by flash column chromatography on silica gel, eluting with diethyl ether:hexane (1:1) to give ethyl (2-(3--cyano-6-methoxy-2-trifluoromethylindol-1-yl)propionate (3.4g) as a colourless solid. ^1H NMR 7.7(d)1H; 7.0(dd)1H; 6.75(d)1H; 5.2(q)1H; 4.2(q)1H; 3.85(s)3H; 1.85(d)3H; 1.15(t)3H.

Step G

A solution of boron tribromide (9.72g, 39mmol) in dichloromethane ($15cm^3$) was added dropwise to a solution of the indole (3.3g, 9.7mmol) in dichloromethane ($35cm^3$) at -70°C, and once the addition was complete, the mixture was allowed to warm to room temperature, and stirred for 3 hours. The mixture was then cooled to 0°C and excess ethanol added dropwise. The solvent was removed in vacuo, ethanol ($30cm^3$) and a couple of drops of concentrated sulphuric acid were added, and the mixture was heated under reflux for 2 hours. The mixture was cooled to room temperature, and the solvent evaporated in vacuo. The residue was taken up in ethyl acetate and washed sequentially with saturated aqueous sodium bicarbonate solution and with water, dried ($MgSO_4$), filtered and the filtrate evaporated to give ethyl 2-(3-cyano-6-hydroxy-2-trifluoromethylindol-1-yl)propionate (2.8g) as a solid. ^1H NMR $CDCl_3$ 7.7(d)1H; 6.95(dd)1H; 6.8(d)1H; 5.3(bs)1H; 5.2(q)1H; 4.2(q)2H; 1.8(d)3H; 1.15(t)3H.

Step H

The indole (1.0g, 3.1mmol) prepared in Step G above, 5-chloro-3,4--difluorobenzotrifluoride (0.67g, 3.1mmol) and potassium carbonate (0.48g, 3.5mmol) were heated together at 100°C in dimethylsulphoxide ($25cm^3$) for 3 hours. The mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The organic extracts were combined, washed with brine, dried ($MgSO_4$), filtered and the filtrate evaporated in vacuo to give Compound No. 16 (1.45g) as an oil.

Compound No. 17 was similarly prepared using appropriate reagents.

EXAMPLE 10

This Example illustrates the preparation of compounds 14 and 15 in Table II.

Sulphuryl chloride ($0.32cm^3$, 4.0mmol) was added to a solution of Compound No. 16 (1.38g, 3.4mmol) in diethyl ether ($20cm^3$) and the reaction mixture was stirred at room temperature for 30 minutes. The mixture was diluted with diethyl ether ($100cm^3$) and washed successively with water ($100cm^3$) and saturated aqueous sodium bicarbonate solution. The ethereal extract was dried ($MgSO_4$), filtered and the filtrate evaporated, and the residue further purified by flash column chromatography on silica gel, eluting with diethyl ether:hexane 1:5 to give Compound No. 14 (0.24g) together with compound No. 15 (1.21g), each as a colourless oil.

EXAMPLE 11

This Example illustrates the preparation of Compound No. 19 in Table II.

Sodium carbonate (0.19g, 2.3mmol) was added to a solution of Compound No. 18 (0.52g, 1.2mmol) in ethanol ($15cm^3$) and water ($5cm^3$) and the mixture stirred at room temperature for 48 hours. More water ($5cm^3$) was added, and the mixture was stirred at room temperature for a further 48 hours. The solvent was concentrated in vacuo and the remaining mixture partitioned between diethyl ether and water. The ethereal extract was washed with brine, dried ($MgSO_4$), filtered and the filtrate evaporated in vacuo. The residue was further purified by flash column chromatography on silica gel, eluting with 15% methanol in dichloromethane to give Compound No. 19 (0.36g) as a colourless solid which was recrystallised from a mixture of diethyl ether and hexane. m.pt > 137°C (dec).

Biological Data

The herbicidal activity of the compounds was tested as follows:

Each compound in the appropriate concentration was incorporated into a 4% emulsion of methylcyclohexanone and 0.4% blend of 3.6 parts Tween 20 and 1 part Span 80. Tween 20 is a Trade Mark for a surface active agent comprising a condensate of 20 molar proportions of ethylene oxide with sorbitan laurate. Span 80 is a Trade Mark for a surface-active agent comprising sorbitan monolaurate. Formulation was effected by dissolving the compound in the requisite amount of solvent/surfactant blend. If necessary, glass beads were added, the total liquid volume adjusted to 5 ml with water, and the mixture shaken to effect complete dissolution of the compound. The formulation so prepared, after removal of beads where necessary, was then diluted to final spray volume (45 ml) with water.

The spray compositions so prepared were sprayed onto young pot plants (post-emergence test) at a rate equivalent to 1000 litres per hectare. Damage to plants was assessed 13 days after spraying by comparison with untreated plants, on a scale of 0 to 9 where 0 is 0% damage, 1 is 1-5% damage, 2 is 6-15% damage, 3 is 16-25% damage, 4 is 26-35% damage, 5 is 36-59% damage, 6 is 60-69% damage, 7 is 70-79% damage, 8 is 80-89% damage and 9 is 90-100% damage.

In a test carried out to detect pre-emergence herbicidal activity, crop seeds were sown at 2 cm depth (i.e. Sb, Ct, Rp, Ww, Mz, Rc, Sy) and weed seeds at 1 cm depth beneath compost and sprayed with the compositions at the rate of 1000 litres per hectare. 20 days after spraying, the seedlings in the sprayed plastic trays were compared with the seedlings in unsprayed control trays, the damage being assessed on the same scale of 0 to 9.

The results of the tests are given in Table IV below.

TABLE IV

COMPOUND NO.	RATE OF APPLICATION kg/ha	PRE-OR POST-EMERGENCE APPLI-CATION	TEST PLANTS (see Table V)																								
			Sb	Rp	Ct	Sy	Mz	Rc	Ww	Pi	Ca	Ga	Am	Bd	Eh	Ip	Ab	Xa	Xs	Av	Al	Ag	Sh	St	Dg	Ec	Ce
1	Pre	1	0	0	0	0	1	0	0	1	0	5	0	0	0	0	0	0	-	0	0	-	0	0	0	0	0
	Post		0	1	0	2	5	0	0	1	9	0	7	0	7	0	0	-	0	0	0	0	6	1	2	0	0
2	Pre	1	0	0	0	2	0	0	0	2	0	-	0	2	2	0	0	0	-	0	0	-	0	0	0	0	0
	Post		4	6	3	5	5	1	0	5	8	-	4	2	6	3	5	-	2	2	2	3	2	2	3	5	2
3	Pre	1	0	0	0	0	0	0	0	0	0	-	0	0	0	0	0	0	-	2	0	-	0	0	0	0	0
	Post		5	6	9	8	6	0	0	8	9	5	9	5	7	5	6	-	7	0	0	0	2	6	0	0	0
4	Pre	1	0	4	2	0	0	0	0	0	0	0	0	2	0	0	4	2	-	0	0	-	-	0	0	0	-
	Post		8	9	7	7	8	2	6	9	9	-	9	8	9	9	9	-	9	6	5	4	8	6	7	4	3

TABLE IV (continued)

COMPOUND NO.	RATE OF APPLICATION kg/ha	PRE-OR POST-EMERGENCE APPLI-CATION	TEST PLANTS (see Table V)																								
			Sb	Rp	Ct	Sy	Mz	Rc	Ww	Pi	Ca	Ga	Am	Bd	Eh	Ip	Ab	Xa	Xs	Av	Al	Ag	Sh	St	Dg	Ec	Ce
5	Pre	1	0	0	0	0	0	0	0	2	5	-	9	3	0	0	0	0	-	2	0	-	0	3	0	0	0
	Post		5	9	9	5	4	3	3	5	9	5	9	5	9	9	9	-	9	4	5	4	7	9	5	4	5
6	Pre	0.25	0	0	0	2	0	0	3	0	0	-	2	0	0	0	0	0	-	0	0	-	0	0	0	0	0
	Post		5	8	9	5	5	2	1	9	9	8	9	5	9	7	9	-	4	2	2	0	7	0	3	2	
7	Pre	1	3	4	0	-	0	3	0	0	5	0	0	0	0	0	4	0	-	0	3	-	0	0	-	0	-
	Post		6	9	9	7	8	3	5	9	9	-	9	7	9	9	9	-	9	3	2	3	9	6	9	3	4
9	Pre	0.25	0	0	0	0	0	0	0	0	0	-	0	0	0	0	0	0	-	0	0	-	0	0	-	0	0
	Post	0.25	3	2	0	1	5	0	1	1	7	0	8	1	5	3	7	0	3	1	0	2	3	0	9	2	2
10	Pre	1	0	0	0	0	0	0	0	0	5	-	5	7	9	0	0	0	-	5	3	-	0	0	0	0	0
	Post	0.25	9	5	8	5	2	0	0	8	7	-	9	3	5	0	5	-	3	2	1	0	0	2	0	0	

TABLE IV (continued)

COMPOUND NO.	RATE OF APPLICATION kg/ha	PRE-OR POST-EMERGENCE APPLICATION	TEST PLANTS (see Table V) Sb	Rp	Ct	Sy	Mz	Rc	Ww	Pi	Ca	Ga	Am	Bd	Eh	Ip	Ab	Xa	Xs	Av	Al	Ag	Sh	St	Dg	Ec	Ce
11	Pre	1	0	0	0	0	0	0	0	0	3	-	0	0	0	0	0	0	-	0	0	-	0	0	0	0	0
	Post	0.25	6	6	9	5	2	2	2	9	7	-	9	7	7	0	9	-	2	3	2	5	0	3	1	0	0
13	Pre	0.25	0	0	-	0	2	0	0	0	0	-	0	4	0	0	0	-	0	0	0	-	0	0	-	0	0
	Post	0.25	4	7	-	3	5	1	2	4	8	4	6	1	2	3	4	-	5	0	0	1	2	3	1	0	1
14	Pre	0.25	0	0	-	0	0	0	0	0	0	-	4	2	-	0	0	-	0	0	0	-	0	0	-	0	0
	Post	0.25	5	9	-	5	8	4	2	5	9	9	9	5	9	6	6	-	9	2	2	3	6	8	7	3	5
15	Pre	0.25	0	0	-	0	2	0	0	0	0	-	0	0	0	0	0	-	0	0	0	-	0	0	-	0	0
	Post	0.25	6	9	-	6	5	2	0	3	9	9	9	3	7	6	6	-	8	2	1	2	3	5	7	2	2

TABLE IV (continued)

COMPOUND NO.	RATE OF APPLICATION kg/ha	PRE-OR POST-EMERGENCE APPLICATION	TEST PLANTS (see Table V)																									
			Sb	Rp	Ct	Sy	Mz	Rc	Ww	Pi	Ca	Ga	Am	Bd	Eh	Ip	Ab	Xa	Xs	Av	Al	Ag	Sh	St	Dg	Ec	Ce	
16	0.25	Pre	0	0	-	0	0	0	0	0	4	-	5	0	0	0	2	-	0	0	0	-	0	0	-	0	0	
	0.25	Post	4	4	-	4	9	2	2	5	9	8	9	3	8	3	5	-	5	4	3	3	9	7	8	2	3	
17	0.25	Pre	0	3	-	0	0	0	0	0	0	-	0	0	3	0	0	-	0	0	0	-	0	0	0	0	0	
	0.25	Post	2	4	-	5	5	4	2	3	5	5	9	3	5	3	3	-	4	4	3	5	3	5	3	0	0	
18	0.25	Pre	0	0	-	0	0	0	0	0	9	-	9	9	0	0	0	-	0	0	0	-	0	0	0	0	0	
	0.25	Post	7	8	-	7	9	2	5	8	9	5	9	9	8	9	9	9	9	9	7	3	7	9	5	2	2	
19	0.25	Pre	0	0	-	0	0	0	0	3	0	-	0	0	0	0	0	-	0	0	0	-	0	0	0	0	0	
	0.25	Post	5	9	-	7	5	2	1	8	9	5	9	5	6	8	9	-	5	2	6	2	6	9	5	2	2	

TABLE IV (continued)

COMPOUND NO.	RATE OF APPLICATION kg/ha	PRE-OR POST-EMERGENCE APPLI-CATION	TEST PLANTS (see Table V)																								
			Sb	Rp	Ct	Sy	Mz	Rc	Ww	Pi	Ca	Ga	Am	Bd	Eh	Ip	Ab	Xa	Xs	Av	Al	Ag	Sh	St	Dg	Ec	Ce
20	0.25	Pre	2	0	-	0	0	0	0	0	5	-	6	-	-	0	3	-	0	0	0	-	0	0	0	0	0
	0.25	Post	6	5	-	5	5	5	3	2	9	4	9	5	0	9	5	-	7	4	2	3	6	2	5	2	5
21	0.25	Pre	2	2	-	0	0	0	0	0	0	0	0	0	0	2	0	-	0	0	0	-	0	0	0	0	0
	0.25	Post	8	9	-	4	5	4	2	5	9	9	9	5	9	6	7	-	-	4	3	5	6	6	5	4	3
22	0.25	Pre	0	0	-	0	0	-	0	0	9	0	9	-	0	0	0	-	0	0	0	-	-	7	-	0	0
	0.0625	Post	6	6	-	7	3	2	1	5	7	9	9	-	9	9	5	-	8	3	3	-	5	5	-	5	0
23	0.25	Pre	6	0	0	0	0	0	0	0	8	2	9	0	0	2	1	-	-	0	0	-	0	9	0	0	0
	0.0625	Post	8	9	6	9	3	5	5	9	8	9	8	9	9	9	9	-	9	6	8	5	8	9	9	9	5

TABLE IV (continued)

COMPOUND NO.	RATE OF APPLICATION kg/ha	PRE-OR POST-EMERGENCE APPLI-CATION	TEST PLANTS (see Table V)																								
			Sb	Rp	Ct	Sy	Mz	Rc	Ww	Pi	Ca	Ga	Am	Bd	Eh	Ip	Ab	Xa	Xs	Av	Al	Ag	Sh	St	Dg	Ec	Ce
24	1	Pre	3	-	3	0	0	0	0	9	9	0	9	4	4	0	9	0	-	0	0	-	2	7	-	0	0
	1	Post	7	9	9	8	9	1	5	9	9	9	9	9	9	9	9	-	9	5	1	3	7	9	9	5	3

TABLE V

Test Plants

Sb - Sugar beet

Rp - Rape

Ct - Cotton

Sy - Soybean

Mz - Maize

Ww - Winter wheat

Rc - Rice

Bd - Bidens pilosa

Ip - Ipomoea lacunosa (pre-emergence)
Ipomoea hederacea (post-emergence)

Am - Amaranthus retroflexus

Pi - Polygonum aviculare

Ca - Chenopodium album

Ga - Galium aparine

Xa - Xanthium spinosum

Xs - Xanthium strumarium

Ab - Abutilon theophrasti

Eh - Euphorbia heterophylla

Av - Avena fatua

Dg - Digitaria sanguinalis

Al - Alopecurus myosuroides

St - Setaria viridis

Ec - Echinochloa crus-galli

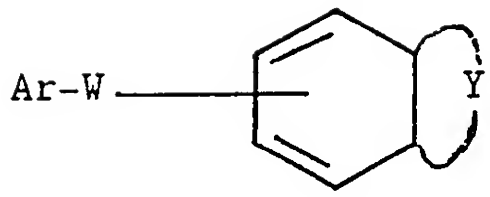
Sh - Sorghum halepense

Ag - Agropyron repens

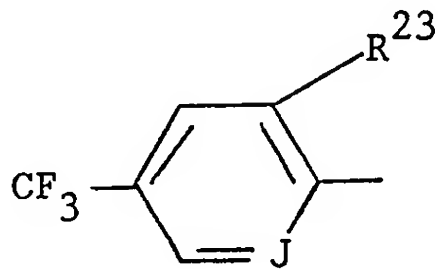
Ce - Cyperus esculentes

CHEMICAL FORMULAE

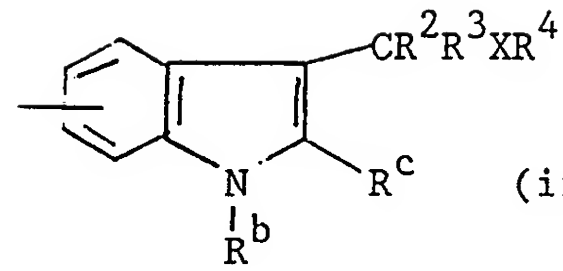
(in descripton)



(I)



(i)



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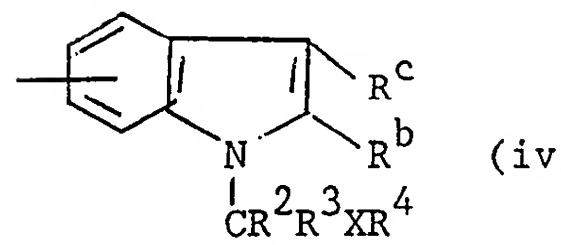
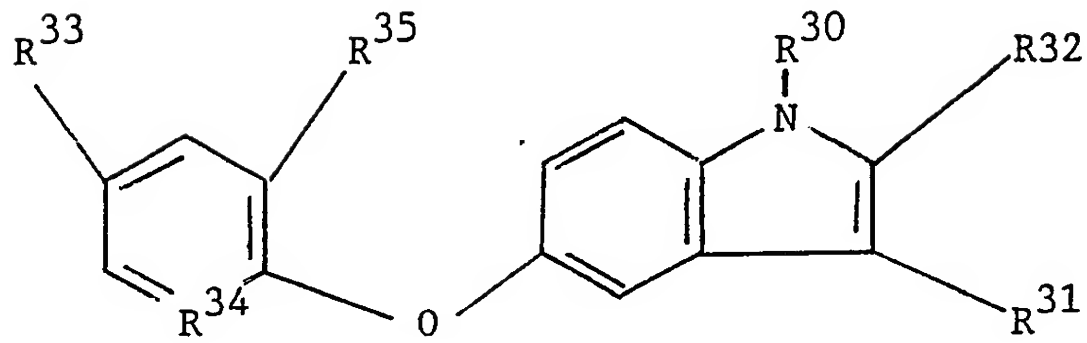
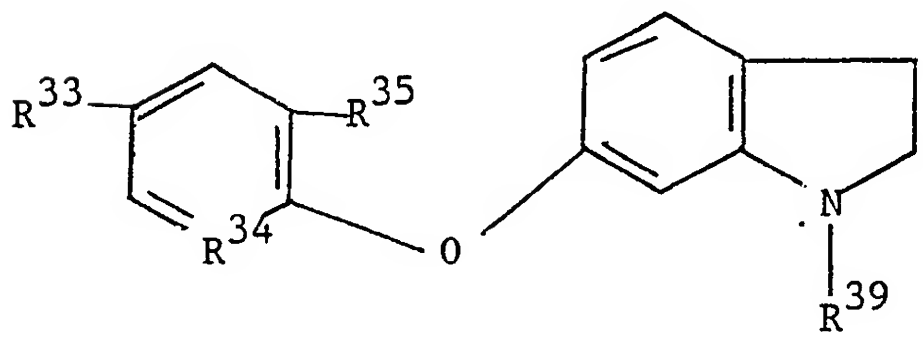


(iv)



(IA)

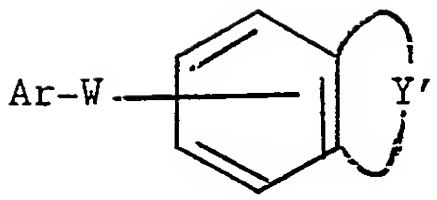
(IB)



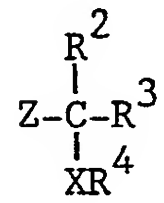
(IC)

CHEMICAL FORMULAE

(in descripton)



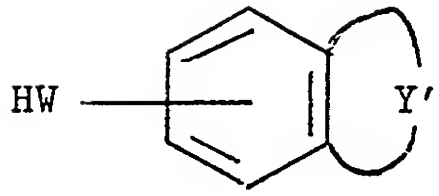
(II)



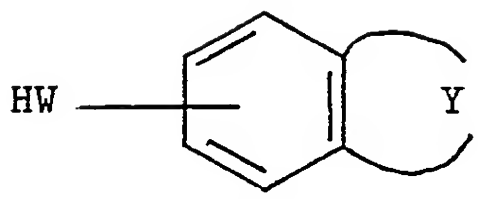
(III)

Ar-Z'

(V)

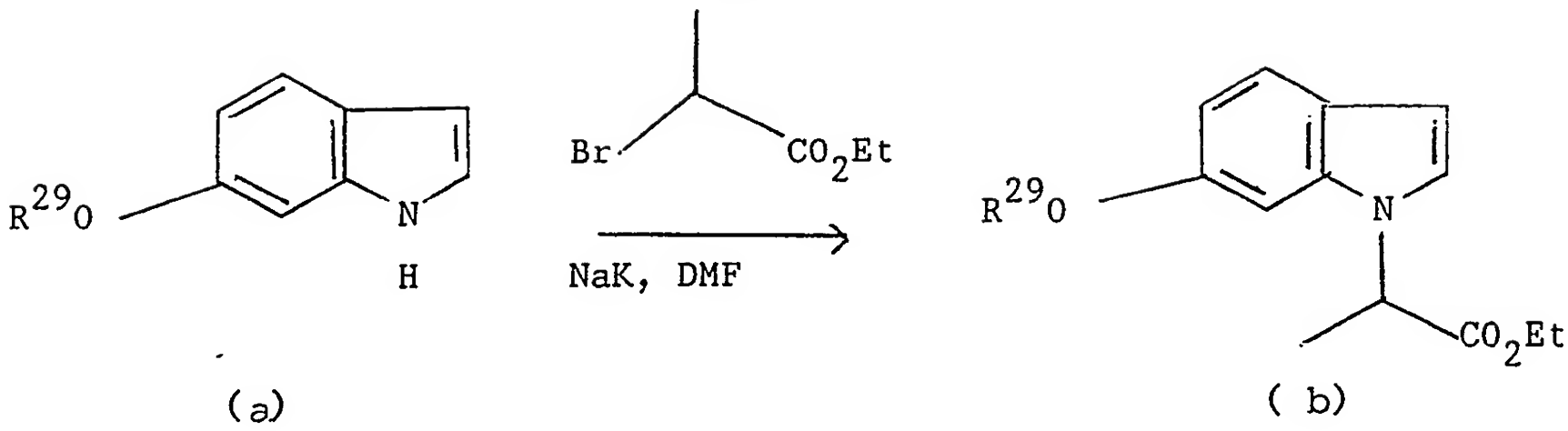


(IV)

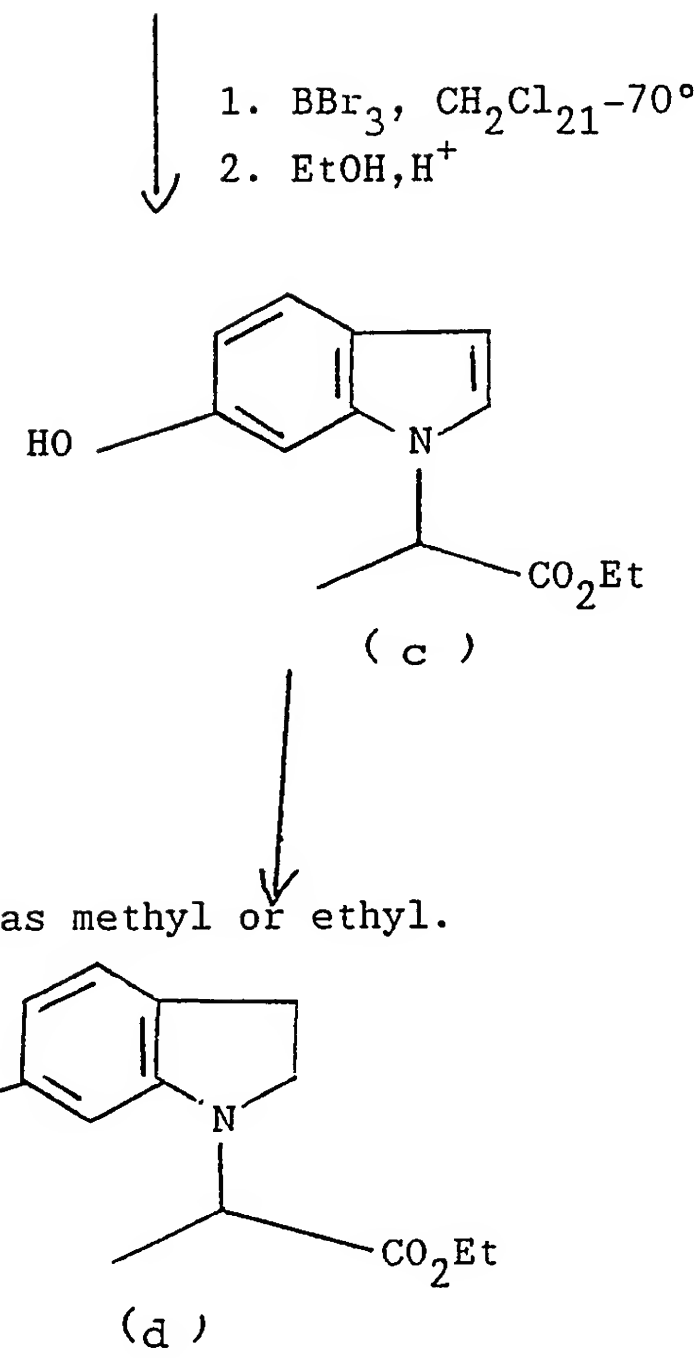


(VI)

Scheme 1



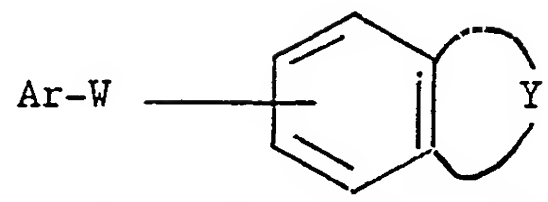
(as described in
W. Leimgruber and A D Batcho,
US Patent 3 732 245, 1973)



where R^{29} is alkyl such as methyl or ethyl.

CLAIMS

1. A compound of formula (I):

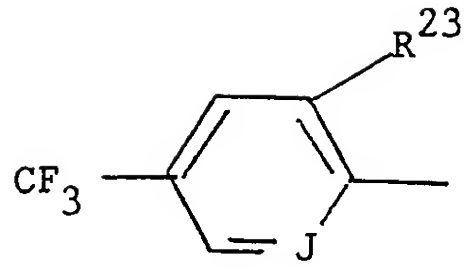


(I)

in which Ar is an optionally substituted aryl or heterocyclic ring system;
W is O or NR^1 where R^1 is hydrogen or lower alkenyl;
Y is a 5 membered saturated or unsaturated ring containing one nitrogen atom, the ring being substituted on at least one carbon or nitrogen atom by a group $CR^2R^3XR^4$ and optionally by one or more additional groups R^a, each R^a being independently selected from OH, optionally substituted alkoxy halogen, optionally substituted alkyl, alkenyl or alkynyl, CO_2R^5, CN, oxo, $S(O)_pR^5$; where p is 0, 1 or 2; X is $(CH_2)_n$, CH=CH, $CH(OR^6)CH_2$, $COCH_2$; where n is 0, 1 or 2; R^2 and R^3 are independently selected from H, optionally substituted alkyl, alkenyl or alkynyl, halogen, NR^7R^8 or R^2 and R^3 together with the carbon to which they are attached form an optionally subitituted alkenyl or cycloalkyl group;
R^4 is CO_2R^9, CN, COR^9, CH_2OR^9, $CH(OH)R^9$, $CH(OR^9)R^{10}$, $CSNH_2$, $COSR^9$, $CSOR^9$, $CONHSO_2R^9$, $CONR^{11}R^{12}$, $CONHNR^{11}R^{12}$, $CONHN^+R^{11}R^{12}R^{13}R^{14-}$, $CO_2^-R^{15}$ or $COON=CR^9R^{10}$;
R^5, R^6, R^9 and R^{10} are independently selected from H or an optionally substituted alkyl, aryl, alkenyl or alkynyl group;
R^7, R^8, R^{11}, R^{12} and R^{13} are independently selected from H or an optionally substituted alkyl, alkenyl, aryl or alkynyl group or any two of R^7, R^8, R^{11}, R^{12} and R^{13} together with the atom to which they are attached form a cycloalkyl or heterocyclic ring;
R^{14-} is an agriculturally acceptable anion; and
$R15^+$ is an agriculturally acceptable cation;

2. A compound according to claim 1 wherein W is oxygen.

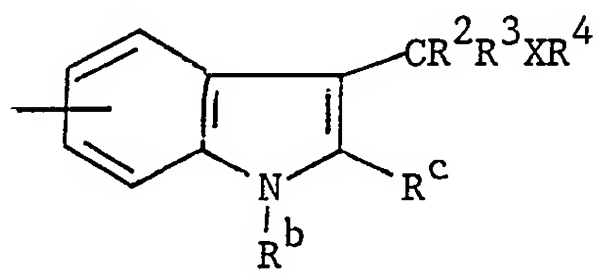
3. A compound according to claim 1 or claim 2 wherein Ar is a group:



in which J is N or R^{24} where R^{23} is H or halo and R^{24} is NO_2 or halo.

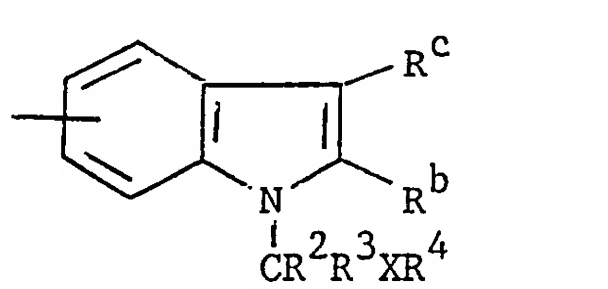
4. A compound according to any one of the preceeding claims wherein Y is an unsaturated ring.

5. A compound according to claim 4 where Y and the ring to which it is fused form a group:



wherein R^b and R^c are independently selected from H or a group R^a and R^a, R^2, R^3, R^4 and X are as defined in relation to Formula (I) in claim 1.

6. A compound according to claim 4 where Y and the ring to which it is fused form a group:

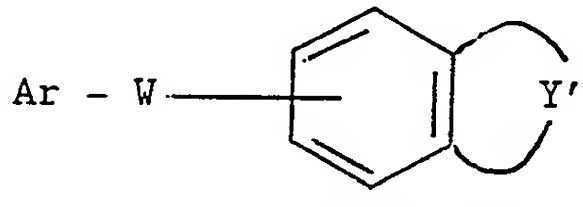


wherein R^b and R^c are independently selected from H or a group R^a and R^a, R^2, R^3, R^4 and X are as defined in relation to Formula (I) in claim 1.

7. A compound according to any of the preceding claims wherein $CR^2R^3XR^4$ is $CHR^{3'}R^{4'}$ where $R^{3'}$ is H or C_{1-3} alkyl and $R^{4'}$ is CO_2R^9.

8. A compound according to claim 7 wherein R^9 is C_{1-6} alkyl.

9. A process for the preparation of compounds of formulae (I) comprising a) reacting a compound of formula (II):



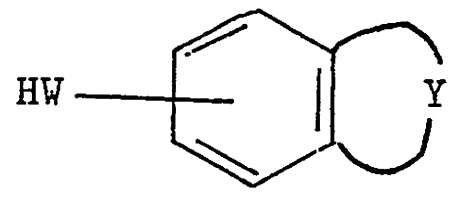
(II)

where Ar and W are as defined in relation to formula (I) in claim 1 and Y′ is as defined for Y in formula (I) except it carries no group $CR^2R^3XR^4$ with a compound of formula (III):

$$Z\text{-}CR^2R^3XR^4 \qquad \text{(III)}$$

where R^2, R^3, R^4 and X are as defined in relation to formula (I) in claim 1 and Z is a leaving group optionally in the presence of a base; or

b) reacting a compound of formula (VI):



(VI)

where W and Y are as defined in relation to formula (I) in claim 1 with a compound of formula (V):

$$Ar\text{-}Z' \qquad \text{(V)}$$

where Ar is as defined in relation to formula (I) in claim 1 and Z′ is a leaving group.

10. A herbicidal composition comprising a compound of formula (I) as defined in claim 1 in combination with a carrier or diluent.

11. A method of killing or controlling the growth of unwanted plants which method comprises applying to the plants or to a locus thereof an effective amount of a compound of formula (I) as defined in claim 1.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number
9204887.5

Relevant Technical fields

(i) UK Cl (Edition K) C2C (CMB, CBD)

(ii) Int CL (Edition 5) C07D 209/18, 209/30

Search Examiner
R HONEYWOOD

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: CAS ONLINE

Date of Search
6 MAY 1992

Documents considered relevant following a search in respect of claims 1-11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1403559 A (SQUIBB) See example 54	1,2,4,7,8
X	CA 113 (3): 23510g J Pharm Sci., 79(3), 266-72	1,2,4,5

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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